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6. AUTHOR(S) Douglas L. Gin				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of California at Berkeley Berkeley, CA 94720			8. PERFORMING ORGANIZATION REPORT NUMBER 96-02	
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13. ABSTRACT (Maximum 200 words) The formation of highly ordered polymer networks using liquid-crystalline (LC) monomers was studied in the context of developing new polymers for use as piezoelectric, dye laser host, and membrane materials. Photopolymerizable, crosslinkable monomers based on thermotropic and lyotropic LC's were sought for these purposes. A precursor to a suitable chiral smectic C monomer for the formation of noncentrosymmetric polymer networks has been synthesized. Two new crosslinkable dye molecules have been developed for alignment and polymerization studies inside LC monomer host matrices. Finally, two lyotropic LC monomers have been developed that result in ordered nanoporous polymer networks when photo-polymerized.				
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**OFFICE OF NAVAL RESEARCH**

Final Technical Report

Publications/Patents/Presentations/Honors/Students Report

for

GRANT: N0014-96-1-0844

PR Number: 96PR05882-00

Scientific Officer: Dr. Kenneth J. Wynne

Morphology and Property Control in Polymer Thin Films  
and Membranes through the Use of Self-Assembling Monomers

by

Douglas L. Gin

University of California, Berkeley  
Department of Chemistry  
Berkeley, CA 94720-1460

January 28, 1997

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Office of Naval Research

Publications/Patents/Presentations/Honors/Students Report

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Principal Investigator: Douglas L. Gin  
Mailing Address: Dept. of Chemistry, University of California, Berkeley, CA 94720  
Phone Number: (510) 642-7756  
Fax Number: (510) 642-8369  
E-mail Address: gin@chemgate.cchem.berkeley.edu  
http address N/A

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| (a) Number of papers submitted to referred journals but not published:                                                                        | 0 |
| (b) Number of papers published in refereed journals                                                                                           | 0 |
| (c) Number of books or chapters submitted but not yet published:                                                                              | 0 |
| (d) Number of books or chapters published:                                                                                                    | 0 |
| (e) Number of printed reports/non-refereed papers:                                                                                            | 1 |
| (f) Number of patents filed:                                                                                                                  | 1 |
| (g) Number of patents granted:                                                                                                                | 0 |
| (h) Number of invited presentations:                                                                                                          | 0 |
| (i) Number of submitted presentations:                                                                                                        | 1 |
| (j) Honors/awards/prizes for contract/grant employees:                                                                                        | 2 |
| (k) Number of full time equivalent graduate students and postdoctoral associates supported during this period, under this R&T project number: |   |

Graduate students:	1.5
Postdoctoral associates	0.5
Female graduate students:	0
Female postdoctoral associates:	0
Minority graduate students:	0
Minority postdoctoral associates:	0
Asian graduate students:	0
Asian postdoctoral associates:	0

- (l) Other funding (see attached list):

(e) Papers Published in Non-Referred Journals:

"Ordered Piezoelectric Networks via a Liquid-Crystalline Monomer Strategy: Synthesis of the LC Monomer," Brian C. Baxter and Douglas L. Gin, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1997**, 38(1), in press.

(f) Patents Filed:

"Highly Ordered Nanocomposites via a Monomer Self-Assembly – In Situ Condensation Approach," Douglas L. Gin, Walter M. Fischer, David H. Gray, and Ryan C. Smith; Application filed Jan. 8, 1997.

(k) Honor/Awards Received:

National Science Foundation Early Faculty Career Development Award  
3M Untenured Faculty Award

(i) Other Funding Received During This Period:

U.S. Dept. of Energy, Center for Advanced Materials, Lawrence Berkeley National Laboratory; (no grant title); \$60,000 this year; total amount: \$60,000 for 1/96–10/96; unconnected to ONR grant.

Raychem Corporation; (unrestricted research gift); \$15,000 this year; total amount: \$15,000 for 10/95–present; unconnected to ONR grant.

ACS Petroleum Research Fund; "Piezoelectric Polymer Networks via Monomer Self-Assembly;" \$10,000 for 9/1/96–8/30/97; total amount: \$20,000 for 9/1/96–8/30/98; partial support of one aspect of the work proposed in ONR grant.

3M Corporation; Untenured Faculty Grant (unrestricted research gift); \$15,000 this year; total amount: \$15,000 for 4/1/96–present; unconnected to ONR grant.

Committee on Research, U. C. Berkeley; "Synthetic Composites with Tunable, Nanometer-Scale Architectures: New Materials via Monomer Self-Assembly;" \$3,000 this year; total amount: \$3,000 for 7/1/96–6/30/97; unconnected to ONR grant.

National Science Foundation; "Highly Ordered Polymeric Materials via Monomer Self-Assembly;" \$65,000 for 6/96–5/97; total amount: \$322,153 for 6/15/96–5/31/00; unconnected to ONR grant.

- (a) Principal Investigator: Douglas L. Gin
- (b) Phone Number: (510) 642-7756
- (c) Cognizant ONR Program Officer: Dr. Kenneth J. Wynne
- (d) Program Objective:

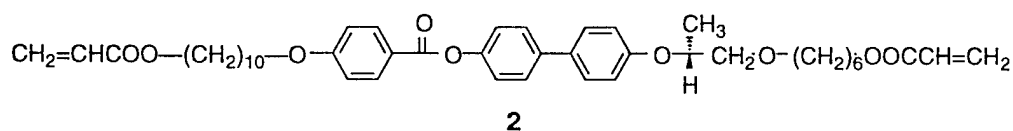
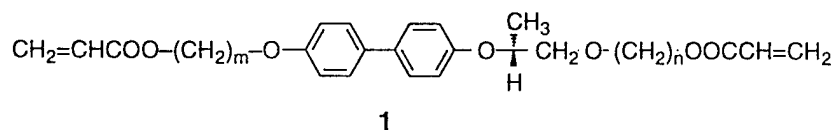
The objective of the research supported by ONR was to develop strategies for controlling small-scale architecture (i.e., order and symmetry) and morphology in polymer films and membranes using monomers with self-assembly properties. The goal of this research was to provide an alternative to current fabrication/processing techniques for controlling these parameters in polymer films and achieve a higher degree of control over architecture on the nanometer-scale. Specifically, this work concentrated on designing liquid-crystalline monomers for use in the construction of new, highly ordered, polymer thin films and membranes. Cross-linkable LC monomers would be used to achieve this objective. It was proposed that the resulting predetermined small-scale order might have profound effects on the bulk properties of three classes of important polymeric materials: piezoelectric polymers, permeable membranes, and polymeric hosts for dye lasers.

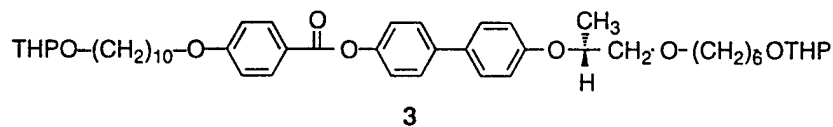
(e) Significant Results and Progress:

Over the brief, six-month tenure of this grant, the following progress has been made in the three sub-areas of the research outlined above:

(1) Ordered Polymer Networks for Piezoelectric Applications

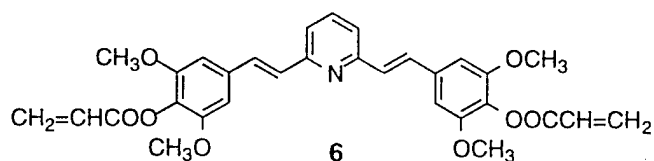
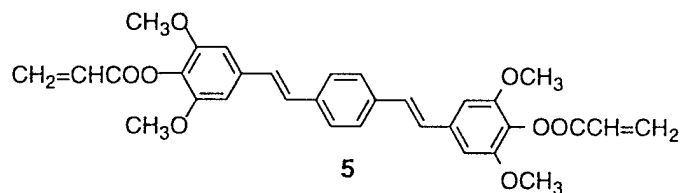
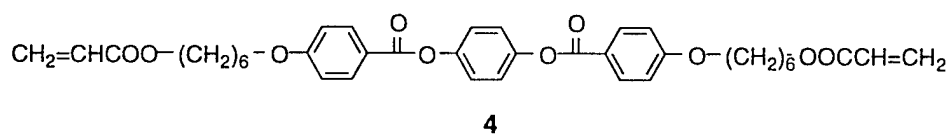
The goal of this work was to design a chiral smectic C difunctional monomer that would spontaneously adopt a tilted, noncentrosymmetric layer phase and then be photopolymerized into a stable, piezoelectric polymer film with retention of the LC order. The resulting network would offer a novel compromise to current single crystal piezoceramics and poled piezoelectric polymers. A single molecular system incorporating intrinsic polymerizability, smectic C LC behavior, and chirality is unprecedented. Our initial goal was to synthesize and study a new class of LC diacrylate monomer **1** that hopefully would provide all these features. We succeeded in synthesizing several examples of **1** with different tail lengths; however they did not prove to be liquid-crystalline. Our assumption was that the central rigid core or the molecule was not sufficiently large to induce liquid-crystallinity. Consequently, we proceeded on the synthesis of a revised monomer **2**. We have just managed to synthesize **3**, the penultimate precursor to **2**, and are currently studying its LC properties. DSC measurements have shown that **3** has two narrow but distinctive LC phases: one between room temperature and 38 °C and the other between 38 °C and 43 °C. We are currently in the midst of determining the identity of these phases using polarized light microscopy and low angle x-ray diffraction.





## (2) Ordered Polymer Network Films as Hosts for Dye Lasers

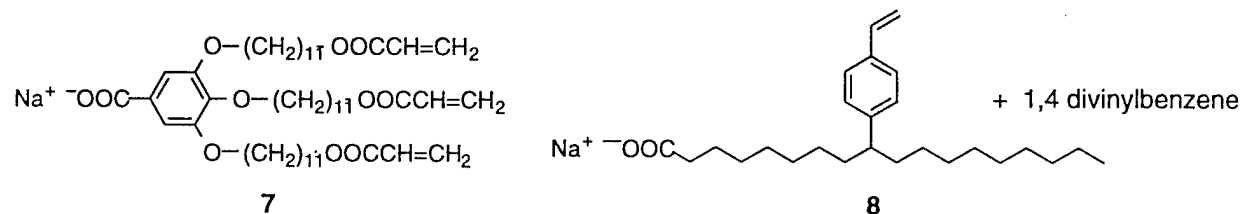
The objective of this aspect of the research program was to design ordered, crosslinked polymer matrices, using new polymerizable LC's, that would (1) address specific performance criteria required for a good dye laser host matrix and (2) introduce new properties to the lasing medium as a result of the inherent order. It was hoped that a heavily crosslinked yet highly ordered polymer matrix with the ability to entrap and align organic laser dyes would enhance stability to thermal damage, lasing efficiency, and perhaps even impart intrinsic polarized emission. We have synthesized several LC monomers described in the literature, such as LC diacrylate **4** (Broer, Hikmet, et al.), to construct ordered networks. We have just begun initial studies incorporating and aligning commercial laser dyes in these LC matrices in order to determine if this host medium will introduce better properties. Parallel to this work, we have also synthesized two novel crosslinkable fluorescent dyes **5** and **6** to determine if (1) these molecules can be aligned and then photopolymerized into the ordered LC network derived from **5**, and (2) to compare their fluorescence behavior in this ordered medium with that in isotropic solution. Experiments with these molecules and networks have just gotten off the ground.



## (3) Morphology and Small-Scale Architectural Control in Polymer Membrane Synthesis

A small portion of the grant money was also used as seed money to initiate a new research project using self-assembling monomers. The objective of this work was to determine if lyotropic (i.e., amphiphilic) LC starting materials could be used to construct new polymeric membranes with control over pore architecture and arrangement in the nanometer regime. These factors are crucial to separation performance and selectivity; however, current methods for making polymer membranes have very little control over these factors. We have used the ONR grant money in part to develop two novel amphiphilic monomers **7** and **8**. Preliminary results have revealed that both lyotropic monomer systems adopt the inverse hexagonal LC phase in the presence of a small amount of water and can be photopolymerized in situ with retention of the

hexagonal channel architecture (Scheme 1). These ordered polymer networks have the potential to be excellent separation membranes because of their regular, aligned nanometer-scale pores. X-ray diffraction and preliminary TEM analysis have shown that the pores are approximately 40 Å in diameter and are extremely uniform in size. Preliminary experiments have also shown that the potential exists for chemically tuning the pore size and aligning the channels homeotropically in thin films. Based on these initial results, a full research project has been developed to synthesize ordered, nanoporous polymer membranes based on these monomers, and a collaboration has been established with a chemical engineering group at North Carolina State University to perform separation studies. This membrane technology has been included as a part of a broad patent application.



**Scheme 1**

